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For: LIGHT EMITTING ELEMENT AND :  
DSIPLAY DEVICE HAVING AN  
INORGANIC PHOSPHOR LAYER

VERIFICATION OF ENGLISH TRANSLATION

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conversant in both the Japanese and English languages and that the English  
translation as attached hereto is an accurate translation of the Japanese  
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Signed this 10th day of March, 2010

Kazuhisa Inaba  
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## TITLE OF THE INVENTION:

## LIGHT EMITTING ELEMENT AND DISPLAY DEVICE

## CLAIMS:

1. A phosphor element comprising:  
an electron hole injection electrode and an electron injection electrode disposed opposite to each other;  
an electron hole transport layer, a phosphor layer, and an electron transport layer stacked in this order from the side of the electron hole injection electrode toward the side of the electron injection electrode, wherein the stacked layers are sandwiched between the electron hole injection electrode and the electron injection electrode, and wherein the phosphor layer includes an inorganic phosphor particle in which at least one part of the surface is covered with an organic material.
2. A phosphor element comprising:  
first and second substrates disposed opposite to each other in which at least one of them is transparent or semi-transparent; and  
an electron hole injection electrode, an electron hole transport layer, a phosphor layer, an electron transport layer, and an electron injection electrode sandwiched in this order between the first and second substrates, and wherein the phosphor layer includes an inorganic phosphor particle in which at least one part of the surface is covered with an organic material.
3. The phosphor element according to claim 1 or 2, wherein the inorganic phosphor particle is a fluorescent substance including a semiconductor host crystal.
4. The phosphor element according to claim 3, wherein the organic

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material is chemically adsorbed to at least one part of a surface of the inorganic phosphor particle.

5. The phosphor element according to claim 4, wherein the organic material is a conductive organic material having an electron hole transporting property and an electron transporting property.

6. The phosphor element according to claim 4, wherein the organic material includes a conductive organic material having an electron hole transporting property and a conductive organic material having an electron transporting property.

7. The phosphor element according to claim 1 or 2, further comprising an electron hole injection layer sandwiched between the electron hole injection electrode and the electron hole transport layer.

8. The phosphor element according to claim 1 or 2, further comprising an electron injection layer sandwiched between the electron injection electrode and the electron transport layer.

9. The phosphor element according to claim 1 or 2, further comprising an electron hole block layer sandwiched between the phosphor layer and the electron transport layer.

10. The phosphor element according to claim 1 or 2, further comprising a thin film transistor connected to the electron hole injection electrode.

11. The phosphor element according to claim 1 or 2, further comprising a thin film transistor connected to the electron injection electrode.

12. The phosphor element according to claim 10 or 11, wherein the thin film transistor is an organic thin film transistor including a thin film formed of an organic material.

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13. A display device comprising:

a phosphor element array in which the plurality of phosphor elements according to any one of claims 10 to 12 are arranged two dimensionally;

a plurality of x electrodes extending parallel to each other in a first direction parallel to a surface of the phosphor element array; and

a plurality of y electrodes extending parallel to each other in a second direction which is parallel to a surface of the phosphor element array and perpendicular to the first direction,

wherein the thin film transistor of the phosphor element array is connected to the x electrode and the y electrode.

DETAILED EXPLANATION OF THE INVENTION

[0001]

UTILIZED FIELD OF THE INVENTION

The present invention relates to a phosphor element which can be used as a luminescent display or various kinds of light sources used for communication or illumination, and a display device using the phosphor element.

[0002]

PRIOR ART

Recently, an electroluminescent (EL) element has been focused on in a flat type of display device. The EL element has characteristics such as a spontaneous illuminant property, excellent visibility, a wide viewing angle, high-speed response and the like. In addition, the EL element which has been developed at present includes an inorganic EL element using an inorganic material as an illuminant and an organic EL element using an organic material

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as an illuminant.

[0003]

According to the inorganic EL element in which an inorganic phosphor such as zinc sulfide and the like is the illuminant, collision excitation occurs between the electrons accelerated in a high electric field of  $10^6$  V/cm and the luminescent center of a fluorescent substance and when it is alleviated, light is emitted. It was found that an element having double insulation structure proposed by INOGUCHI in 1974 had high luminance and long life, and it has been put to practical use as an in-car display and the like.

[0004]

The inorganic fluorescent substance is provided such that an inorganic material which becomes a luminescent center is doped in a host crystal including an insulator crystal in general. Since the host crystal is chemically stable, the inorganic EL element is highly reliable and has a long life of 30,000 hours or more. However, the electrons are not likely spread in the insulator crystal, and it is charged because the injected electrons are accumulated on the surface. As a result, since the following injected electrons are repelled, highly energized electrons as an excitation source need to collide. Therefore, although the inorganic EL element has high reliability and a long life, it needs a high alternating voltage for driving, so that it cannot be driven in an active matrix using a thin film transistor. Consequently, it is not put to practical use as a display device in a television and the like.

[0005]

In addition, according to a technique disclosed in Japanese Patent Publication No. 54-8080, emission luminance is improved by doping a transition

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metal element or a rare-earth element such as Mn, Cr, Tb, Eu, Tm, Yb and the like in a phosphor layer including ZnS mainly but an average luminance is less than  $400\text{cd/m}^2$ , which is not sufficient as the display device in television and the like.

[0006]

Meanwhile, according to the organic EL element in which the organic material is the illuminant, electron holes and electrons injected from electrodes form exciters and light is emitted when they transit to the ground state. A two-layer element in which an electron hole transport layer and an organic phosphor layer are sequentially stacked, which was proposed by Tang etc. at 1987, can emit light whose luminance is  $1,000\text{cd/m}^2$  or more at a driving voltage of 10V or less, as described in NPL 1. This triggers active research and development for the organic EL element up to now.

[0007]

The organic EL element which is studied at present in general will be described with reference to Fig. 5. An organic EL element 50 is formed such that a transparent electron hole injection electrode 52, an electron hole transport layer 53, a phosphor layer 56 and an electron injection electrode 58 are sequentially stacked on a transparent substrate 51. In addition, an electron hole injection layer may be provided between the electron hole injection electrode 52 and the electron hole transport layer 53, an electron transport layer 57 may be provided between the phosphor layer 56 and the electron injection electrode 58, an electron hole block layer may be provided between the phosphor layer 56 and the electron transport layer 57, or an electron injection layer may be provided between the electron transport layer

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and the electron injection electrode 58.

[0008]

The electron hole injection electrode includes ITO (indium tin oxide) film and the like which is a transparent conductive film. In order to improve transparency or lower resistivity in the ITO film, it is formed by a sputtering method, an electron beam evaporation method, an ion plating method and the like.

[0009]

The electron hole transport layer is formed of a diamine derivative used by Tang etc. such as N, N'-bis (3-methylphenyl) -N, N'-diphenylbenzidine (TRD) and the like. The material is excellent in transparency in general and it is almost transparent even when its film thickness is 80 nm.

[0010]

The phosphor layer is formed of an electron transporting luminescent material such as tris (8-quinolinolato) aluminum (Alq3) and the like so as to be several tens of nm in thickness by vacuum evaporation similar to the report by Tang etc. in general. In order to implement various luminescent colors, a so-called double hetero structure in which the phosphor layer is relatively thin and the electron transport layer is laminated by about 20 nm may be employed.

[0011]

As the electron injection electrode, alloy of metal having a low work function and a low electron injection barrier and stable metal having a relatively great work function, such as a MgAg alloy or an AlLi alloy proposed by Tang etc., or a laminated electrode of various electron injection layers of LiF and Al and the like is used in many cases.



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[0012]

In addition, an organic EL display device using a low-temperature polysilicon thin film transistor in driving each pixel is known, as described in NPL 2.

[0013]

NON PATENT LITERATURE 1:

Applied Physics Letters, 51, 1987, P913

NON PATENT LITERATURE 2:

Journal of the Society for Information Display, vol.8, No.2, p93-97

[0014]

According to the conventional organic EL element, there is a defect such that a molecular bonding of the organic material which becomes the illuminant is cut because of an impressed electric field or light irradiation and the like under existence of water or oxygen, so that luminescent performance is lowered. Therefore, it cannot be practically used in continuous driving or it does not have good keeping quality. To solve the above problem, as disclosed in Japanese Patent Laid-open Publication No. 2003-59665, a hybrid organic EL element using a high-reliable inorganic material as the illuminant has been proposed.

[0015]

## PROBLEM TO BE SOLVED BY THE INVENTION

In a case where the phosphor element is used as a display device in television and the like, it has to have a life of 30,000 hours at least. In addition, it has to be driven at a low voltage so that active matrix driving can be driven by a thin film transistor. According to the conventional organic EL element,

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although it can be driven at a low voltage, it does not have a long life because the organic material is used as the illuminant. Meanwhile, according to the conventional inorganic EL element, although it has a long life, it needs a high voltage at the time of driving. In addition, in the case of the hybrid phosphor element conventionally proposed, although the inorganic fluorescent substance can emit light at a DC low voltage, excellent luminescent characteristics and reliability of the inorganic phosphor are not advantageously used. Thus, it is difficult to satisfy high luminance, high reliability and a long life at the same time regardless of the material of the illuminant.

[0016]

Thus, it is an object of the present invention to provide a phosphor element having high luminance and a long life which can be driven at low voltage, and a display device using the above phosphor element.

[0017]

#### MEANS FOR SOLVING THE PROBLEM

A phosphor element according to the present invention includes an electron hole injection electrode and an electron injection electrode disposed opposite to each other, an electron hole transport layer, a phosphor layer, and an electron transport layer stacked in this order from the side of the electron hole injection electrode toward the side of the electron injection electrode. The stacked layers are sandwiched between the electron hole injection electrode and the electron injection electrode. The phosphor layer includes an inorganic phosphor particle in which at least one part of the surface is covered with an organic material.

[0018]

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A phosphor element according to the present invention includes first and second substrates disposed opposite to each other in which at least one of them is transparent or semi-transparent, and an electron hole injection electrode, an electron hole transport layer, a phosphor layer, an electron transport layer, and an electron injection electrode sandwiched in this order between the first and second substrates. The phosphor layer includes an inorganic phosphor particle in which at least one part of the surface is covered with an organic material.

[0019]

Furthermore, it is preferable that the inorganic phosphor particle is a fluorescent substance including a semiconductor host crystal.

[0020]

Still furthermore, the organic material may be provided on at least one part of the surface of the inorganic phosphor particle by chemical adsorption. In addition, the organic material may be a conductive organic material having an electron hole transporting property and an electron transporting property. In addition, the organic material may include a conductive organic material having an electron hole transporting property and a conductive organic material having an electron transporting property.

[0021]

Still furthermore, an electron hole injection layer sandwiched between the electron hole injection electrode and the electron hole transport layer may be further provided.

[0022]

In addition, an electron injection layer sandwiched between the electron

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injection electrode and the electron transport layer may be provided.

[0023]

In addition, an electron hole block layer sandwiched between the phosphor layer and the electron transport layer may be provided.

[0024]

Still furthermore, a thin film transistor connected to the electron hole injection electrode or the electron injection electrode may be provided. In addition, the thin film transistor may be an organic thin film transistor including a thin film formed of an organic material.

[0025]

An active matrix display device according to the present invention includes a phosphor element array in which the plurality of phosphor elements are arranged two dimensionally, a plurality of x electrodes extending parallel to each other in a first direction parallel to a surface of the phosphor element array, and a plurality of y electrodes extending parallel to each other in a second direction which is parallel to a surface of the phosphor element array and perpendicular to the first direction. The thin film transistor of the phosphor element array is connected to the x electrode and the y electrode.

[0026]

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, a phosphor element and a display device using the phosphor element according to embodiments of the present invention will be described with reference to the accompanying drawings. In addition, the same reference numerals are allotted to substantially the same components in the drawings.

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[0027]

(First Embodiment)

A phosphor element according to a first embodiment of the present invention will be described with reference to Fig. 1. Fig. 1 is a sectional view showing the phosphor element and perpendicular to its light emission surface. In the phosphor element 10, an inorganic phosphor particle 4 is used as an illuminant. The phosphor element 10 includes a transparent substrate 1, an electron hole injection electrode 2 provided on the transparent substrate 1, an electron injection electrode 8 provided so as to be disposed opposite to the electron hole injection electrode 2, and a phosphor layer 6 sandwiched between the transparent electron hole injection electrode 2 and the electron injection electrode 8. The phosphor layer includes the inorganic phosphor particle 4, which includes an electron transporting organic material 5 chemically adsorbed to its surface. More specifically, the phosphor element 10 includes an electron hole transport layer 3 between the electron hole injection electrode 2 and the phosphor layer 6, and an electron transport layer 7 between the phosphor layer 6 and the electron injection electrode 8. In addition, light is emitted from the side of the transparent substrate 1 as shown by an arrow in the drawing. Furthermore, addition to the above constitutions, an electron hole injection layer and/or a conductive layer may be provided between the electron hole injection electrode 2 and the electron hole transport layer 3, for example. In addition, an electron hole block layer and /or a conductive layer may be provided between the phosphor layer 6 and the electron transport layer 7, for example. Still furthermore, an electron injection layer and /or a conductive layer may be provided between the electron transport layer 7 and the electron injection

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electrode 8, for example.

[0028]

Next, each component of the phosphor element 10 will be described in detail. First, a description will be made of the transparent substrate 1. The transparent substrate 1 may only have to support each layer formed thereon. In addition, the transparent substrate 1 may be formed of a transparent or a semi-transparent material so that light generated in the inorganic phosphor layer 6 can be emitted. As the transparent substrate 1, a glass substrate such as Corning 1737 or a resin film formed of polyester or the like may be used. In addition, a non-alkali glass, a ceramics substrate or a silicon substrate may be used so that alkali ion and the like contained in normal glass may not affect the phosphor element. In addition, alumina and the like may be coated on a glass surface as an ion burrier layer. As the resin film, a material having durability, flexibility, transparency, electric insulation and moisture resistance, such as a combination of polyethylene terephthalate series or polychlorotrifluoroethylene series and nylon 6 or fluorocarbon resin material or the like can be used. In addition, when the light is emitted from the surface of the electron injection electrode 8, the transparent substrate 1 is not necessarily transparent.

[0029]

Next, a description will be made of the electron hole injection electrode 2. As the electron hole injection electrode 2, metal having transparency and high work function is used, and especially ITO (indium tin oxide) film is used. In addition, SnO<sub>2</sub> Ni, Au, Pt, Pd, Cr, Mo, W, Ta, Nb and the like or an allow of these can be used. Furthermore, a conductive resin such as polyaniline may be used. The ITO film can be formed by a sputtering method, an electron

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beam evaporation method, ion plating method and the like in order to improve its transparency or to lower its electric resistivity. In addition, after the film is formed, a surface processing such as plasma processing may be performed in order to control the electric resistivity or the work function. Although a film thickness of the electron hole injection electrode 2 is determined by a required sheet resistance value and visible light transmission coefficient, since a drive current density is relatively high in the phosphor element 10 and a wiring resistance becomes a problem, it is not less than 100 nm to reduce the sheet resistance value in many cases. In addition, when at least one electrode of the electron hole injection electrode 2 and the electron injection electrode 8 is made transparent or semi-transparent, surface emission can be implemented. In addition, if surface emission is implemented from the surface of the electron injection electrode 8, it is not necessary to use transparent electron hole injection electrode 2. Still furthermore, when both electron hole injection electrode 2 and electron injection electrode 8 are made transparent or semi-transparent, a both-surface emission type of phosphor element can be provided.

[0030]

Next, a description will be made of the electron hole transport layer 3. As the electron hole transport layer 3, an organic material including an electron hole transporting property is used, which includes two main types such as a low-molecular material and a high-molecular material. The low-molecular material including the electron hole transporting property includes a diamine derivative and especially a two-structure diamine derivative of Q1-G-Q2 disclosed in Japan Patent No. 2037475 used by Tang etc. such as N,N'-bis

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(3-methylphenyl)-N,N'-diphenylbenzidine (TPD), or N,N'-bis ( $\alpha$ -naphthyl)-N,N'-diphenylbenzidine (NPD), and the like. In addition, Q1 and Q2 are groups having a nitride atom separately and at least three carbon chains (at least one of them is an aromatic group), and G is a connecting group including a cycloalkylene group, an arylene group, an alkylene group or carbon-carbon connection. In addition, as the high-molecular material including the electron hole transporting property, there are  $\pi$ -conjugated polymer, or  $\sigma$ -conjugated polymer, and a low-molecular polymer which incorporates a molecular structure showing the electron hole transporting property in a molecular chain, in which an arylamines compound and the like are incorporated. More specifically, it includes a poly-para-phenylene vinylene derivative (PPV derivative), polythiophene derivative (PAT derivative), polyparaphenylene derivative (PPP derivative), polyalkylphenylene (PDAF), a polyacetylene derivative (PA derivative), a polysilane derivative (PS derivative) and the like. Especially, poly-N-vinylcarbazole (PVK) shows high hole mobility such as  $10^{-6}$  cm<sup>2</sup>/Vs. As another example, there are polyethylenedioxythiophene (PEDOT), polystyrenesulfonate (PSS), polymethylphenylsilane (PMPS) and the like.

[0031]

In addition, a form in which molecules of the low-molecular material including the electron hole transporting property is dispersed in non-conductive polymer can be taken. As a concrete example of the molecular dispersion, there is an example in which molecules of tetraphenyldiamine (TPD) are dispersed in polycarbonate in high concentration and its hole mobility is about  $10^{-4}$  to  $10^{-5}$  cm<sup>2</sup>/Vs.

[0032]



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A method of forming the electron hole transport layer 3 includes a vacuum evaporation method in the case of the low-molecular material, an inkjet method, a dipping method, a spin coat method, and other various methods in the case of the high-molecular material.

[0033]

Next, a description will be made of the phosphor layer 6. The phosphor layer 6 includes inorganic phosphor particles 4 in which at least a part of its surface is covered with the conductive organic material 5. It is preferable that the conductive organic material 5 may be chemically adsorbed to a surface of the inorganic phosphor particle 4.

[0034]

As a fluorescent substance constituting the inorganic phosphor particle 4, it is preferable that it is not absorbed in a visible light region and has low electric resistance. The fluorescent substance is so constituted that one or more metal elements selected from transition metal ion, such as  $Mn^{2+}$ ,  $Cr^{3+}$ ,  $Cu^{+}$ ,  $Ag^{+}$ , and rare earth metal ion, such as  $Eu^{3+}$ ,  $Eu^{2+}$ ,  $Tb^{3+}$ ,  $Ce^{3+}$ ,  $Nd^{3+}$ ,  $Pr^{3+}$  and the like are added as an activator agent in the center of one or more host crystals including semi-insulating semiconductor in general. In addition, non-metal element such as Cl, Al or I may be added together. As the host crystal, there are sulfide, oxide series. Regarding the sulfide, there are group XII - XVI compound semiconductors ( $ZnS$ , for example), group II - XVI compound semiconductors ( $CaS$ , for example), gallium sulfide ( $Ga_2S_3$ , for example), aluminum sulfide ( $Al_2S_3$ , for example). Meanwhile, regarding the oxide series, there are metal oxide ( $ZnO$ , for example), metal composite oxide ( $Zn_2SiO_4$ , for example). The single host crystals having low resistance include

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an oxide or a composite oxide containing at least one element selected from a group Zn, Ga, In, Sn and Ti. As respective examples of the fluorescent substance, there are ZnO : Zn (luminescent color is Blue-Green), (Zn, Mg) O : Zn (Blue), ZnGa<sub>2</sub>O<sub>4</sub> : Mn<sup>2+</sup> (Green), In<sub>2</sub>O<sub>3</sub> : Eu<sup>3+</sup> (Red), SnO<sub>2</sub> : Eu<sup>3+</sup> (Red), CaTiO<sub>3</sub> : Pr<sup>3+</sup> (Red) and the like. Furthermore, in the case of the host crystal having relatively high resistance such as ZnS, the above host crystal having low resistance such as ZnO or In<sub>2</sub>O<sub>3</sub> may be mixed to lower the resistance. In addition, the activator agent has an appropriate concentration in general, and emission intensity is reduced because of concentration quenching if the concentration becomes higher than a certain level. Because it is thought that excitation energy is transmitted from one direction to the other because of quantum resonance in the center of the emission, so that it reaches a non-emission part.

[0035]

Next, a description will be made of the conductive organic material 5 chemically adsorbed to the surface of the inorganic phosphor particle 4. The conductive organic material 5 may only have to include the electron transporting property and hole transporting property, and may be formed of one or more materials. In addition, the conductive organic material includes a low-molecular material and a high-molecular material.

[0036]

The organic material having a hole transporting property may be formed of the same one used in the above electron hole transporting layer 3.

On the other hand, the low-molecular material including the electron transporting property includes an oxadiazole derivative, a triazole derivative, a

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styryl benzene derivative, a silole derivative, 1,10-phenanthroline derivative, a quinolinol series metal complex, and the like or their dimer or trimer. The following material may be used, that is, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD); 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ); 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP); and tris (8-quinolinolato) aluminum (Alq3). In addition, the high-molecular material including the electron transporting property includes poly-[2,6-(2-cyano-6-methylheptyloxy)-1,4-phenylene] (CN-PPV), polyquinoxaline, and a low-molecular polymer incorporating a molecular structure which shows the electron transporting property, in a molecular chain.

[0037]

In addition, as a material including both electron hole transporting property and electron transporting property, a bipolar high-molecular material which copolymerizes a unit including the electron hole transporting property and a unit including the electron transporting property in their molecular chains may be used. For example, there is P (VK-co-OXD) which randomly copolymerize 9-vinylcarbazole as the electron hole transporting unit and oxadiazole vinylmonomer as the electron transporting unit, PTPDOXD in which TPD as the electron hole transporting unit and oxadiazole as the electron transporting unit are alternately arranged and the like.

[0038]

Next, a description will be made of a method of chemically adsorbing the conductive organic material to the surface of the inorganic phosphor particle

4. The chemical adsorption method includes a method in which a carboxyl

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group (-COOH) is introduced to the conductive organic material 5, and it is esterified to a hydroxyl group on the surface of the inorganic phosphor particle 4 and solidified. Although the esterifying process can be performed by melting or diffusing the conductive organic material 5 in a solvent and soaking the inorganic phosphor particle 4 in the solved or diffused liquid, the present invention is not limited to this. Thus, the inorganic phosphor particle 4 on which the conductive organic material 5 is adsorbed can be formed. In addition, instead of the carboxyl group, a thiocarboxyl group, (-CSOH), a dithiocarboxyl group (-CSSH), a sulfo group (-SO<sub>3</sub>H), a sulfino group (-SO<sub>2</sub>H), a sulfeno group (-SOH), a phosphono group (-PO(OH)<sub>2</sub>), a phosphine group (-PH<sub>2</sub>O<sub>2</sub>), a mercapto group (-SH), a trimetoxylyl group (-Si(OCH<sub>3</sub>)), a trichlorosilyl group (-SiCl<sub>3</sub>), an amid group (-CONH<sub>2</sub>) and an amino group (-NH<sub>2</sub>) may be used. In addition, after the conductive organic material 5 is adsorbed to the surface, a post-processing such as heating, acid or base processing may be performed. The present invention is not limited to the above-mentioned methods.

[0039]

In addition, the chemical adsorption between the conductive organic material 5 and the surface of the inorganic phosphor particle 4 protects the inorganic phosphor particle 4 from being influenced by water and the like and it is effective in improving chemical stability and a handling ability.

[0040]

According to a method of forming the phosphor layer 6 including the inorganic phosphor particles 4, the inorganic phosphor particles 4 are diffused in an organic solvent and the like which does not fuse the conductive organic

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material 5, and various applying method such as the inkjet method, the dipping method, the spin coat method and the like can be used. Furthermore, the phosphor layer 6 may contain a surface-active agent as a diffusion auxiliary agent. Thus, diffusion stability is improved and uniformity in the phosphor layer 6 is improved.

[0041]

A description will be made of the electron transport layer 7. The electron transport layer 7 is formed of an organic material including an electron transporting property and it may be formed of the same one used in the above electron transporting organic material 5.

[0042]

A method of forming the electron transport layer 7 includes a vacuum evaporation method in the case of the low-molecular material, and an inkjet method, a dipping method, a spin coat method, various kinds of methods in the case of the high-molecular material.

[0043]

A description will be made of the electron injection electrode 8. The electron injection electrode 8 may be formed of an alloy of alkali metal or alkaline-earth metal in which the work function is small and electron injection barrier is few, and stable metal in which the work function is relatively great such as Al or Ag. The electron injection electrode 8 formed of the alloy is stable and its electron injection is easy. The electron injection electrode 8 may be formed of MgAg, AlLi and the like. Another electron injection electrode 8 includes various kinds of electrodes having a constitution in which a metal thin film having small work function is formed on the side of the organic layer and a

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metal film formed of stable metal is stacked on the film as a protection electrode, or a constitution in which a thin film of LiF or a  $\text{Al}_2\text{O}_3$  is formed and then an Al film is formed a little thickly, for example. In addition, when the light is emitted from the side of the electron injection electrode 8, it is to be transparent or semi-transparent in addition to the above constitution. For example, the electron injection electrode 8 is formed such that a thin film of MgAg having a thickness of about 10 nm is provided, and then a protection layer is provided thereon.

[0044]

Next, a description will be made of a mechanism of emission of the phosphor element 10 formed as described above. The conductive organic material 5 is a material having carriers (electron hole and electron) transporting property alone and it has a molecular structure in which  $\pi$  electron cloud to transport electrons is largely spread. As describe above, since the conductive organic material 5 is chemically adsorbed to the surface of the inorganic phosphor particle 4 and conductivity of the host crystal is high, the spread of the  $\pi$  electron cloud of the conductive organic material 5 affects up to the surface of the inorganic phosphor particle 4 and carriers are injected without being hindered by the injection barrier. The following two processes are thought in the course of emission. That is, according to the first process, the carriers injected in the inorganic phosphor particles 4 are moved to the vicinity of the emission center of the host crystal and the electron hole is captured by an acceptor level and the electrons are captured by a donor level, and light is emitted when they are recombined. According to the second process, electron transition of rare-earth ion and the like which is activated by movement of

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recombination energy in the emission center is generated and the light is emitted when it is alleviated. It is thought that the first and second emission processes are mixed in practice.

[0045]

(Second Embodiment)

A phosphor element according to a second embodiment of the present invention will be described with reference to Fig. 2. Fig. 1 is a perspective view showing an electrode constitution of the phosphor element 20. The phosphor element 20 further includes a thin film transistor 11 connected to a transparent electron hole injection electrode 2. An x electrode 12 and a y electrode 13 are connected to the thin film transistor 11. In addition, when the thin film transistor is used, the phosphor element 20 has a memory function. As this thin film transistor 11, low-temperature polysilicon or amorphous silicon thin film transistor and the like may be used. Furthermore, it may be an organic thin film transistor constituted by a thin film formed of an organic material.

[0046]

(Third Embodiment)

A display device according to a third embodiment of the present invention will be described with reference to Figs. 3 and 4. Fig. 3 is a schematic view showing an active matrix of the display device 30 which is constituted by x electrodes 12 and y electrodes 13 which intersect with each other. Fig. 4 is a sectional view showing the display device 30 and parallel to the x electrodes 12 and perpendicular to its emission surface. The display device 30 is an active matrix display device having a thin film transistor 11. The active matrix display device 30 includes a phosphor element array in which

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a plurality of phosphor elements shown in Fig. 2 are arranged two dimensionally, the plurality of x electrodes 12 extending parallel to each other in a first direction which is parallel to a surface of the phosphor element array, and the plurality of y electrodes 13 extending parallel to each other in a second direction which intersects with the first direction at right angles. The thin film transistor 11 in the phosphor element connects the x electrode 12 to the y electrode 13. The phosphor element specified by the pair of x electrode 12 and y electrode 13 becomes a pixel. According to the active matrix display device 30, as described above, a phosphor layer 6 constituting the phosphor element of each pixel includes inorganic phosphor particles 4 having a conductive organic material 5 on its surface. Thus, since the carrier can be effectively injected to the inorganic phosphor particles 4 and the inorganic phosphor particles 4 can emit light, the display unit can be driven at the low voltage and has a long life. In addition, when the inorganic phosphor particles 4 are arranged in each of the pixels 41a(R), 41b(G), and 41(C) depending on its luminescent color, there can be provided a full-color display device using the three primary colors. In addition, the inorganic fluorescent substance 4 which emits one color may be used in every pixel 41, and a color conversion layer and the color filter may be further provided ahead of the phosphor direction. Thus, there can be provided a full-color display device using the three primary colors according to another example.

[0047]

Next, a description will be made of a manufacturing method of the active matrix display device 30 with reference to Fig. 4. Similar to the phosphor element 10 in the first embodiment, the thin film transistor 11 is



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formed on a transparent substrate 1 and then a transparent electron hole injection electrode 2 is formed and then an electron hole transport layer 3, a phosphor layer 6 and an electron transport layer 7 are sequentially formed by the inkjet method, for example. Then, an electron injection electrode 8 is formed by the vacuum evaporation method, for example. In the case of the color display device, when the phosphor layer 6 is formed, the pixel 41a (R), the pixel 41b (G), and the pixel 41c (B) are formed so as to be separated by color by applying a solution containing the inorganic phosphor particles 4 of RGB so as to align with a pixel pitch using the ink jet method, for example. Before this step, a pixel separating region 42 which separates each pixel may be formed. In addition, the above manufacturing method is just one example and the present invention is not limited to this.

[0048]

## EXAMPLE

Next, a description will be made further in detail with reference to concrete working examples.

[0049]

(Working example 1)

A phosphor element according to a working example 1 of the present invention will be described with reference to Fig. 1. Since the phosphor element has the same constitution as that of the phosphor element 10 according to the first embodiment, a description of its constitution will be omitted. According to this phosphor element, a commercially available glass substrate having an ITO film was used as the transparent substrate 1 on which the transparent electron hole injection electrode 2 was formed. In addition, ZnO:

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Zn was used in the inorganic phosphor particle 4. Since it is thought that Zn excess part exists as a lattice defect in ZnO and this lattice defect functions as the emission center, an activator agent such as the rare-earth ion and the like is not needed. As the conductive organic material 5 to be chemically adsorbed on the surface of the inorganic phosphor particle 4, an  $\alpha$ -NPD derivative and a PBD derivative were used. In addition, PEDOT was used in the electron hole transport layer 3, Alq3 was used in the electron transport layer 7 and Al was used in the electron injection electrode.

[0050]

Next, a description will be made of a manufacturing method of the phosphor element. The phosphor element is manufactured by the following steps.

- (a) The commercially available glass substrate having the ITO film was prepared as the transparent substrate 1 on which the transparent electron hole injection electrode 2 was formed. Then, ultrasonic cleaning was performed on this using alkali detergent, water, acetone, and isopropyl alcohol (IPA). Then, this was taken out of the boiling IPA solution and dried and cleaned by UV/O<sub>3</sub>.
- (b) Then, PEDOT is dissolved with chloroform and applied to the glass substrate having the ITO film by the spin coat method to form the electron hole transport layer 3. The film thickness thereof was 100 nm.
- (c) The inorganic phosphor particle 4 to which the conductive organic material 5 was chemically adsorbed on the surface was diffused in ethanol using ultrasound and applied to the electron hole transport layer 3 by the spin coat method to form the phosphor layer 6. The film thickness thereof was 150 nm.

[0051]

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Here, a description will be made of a manufacturing method of the inorganic phosphor particle 4 to which the conductive organic material 5 is chemically adsorbed.

(1) First, fine crystal particle powder of ZnO : Zn is used as the inorganic phosphor particle and the fine crystal particle powder of ZnO : Zn is diffused in ethanol using an ultrasonic stirring apparatus.

(2) Then, an  $\alpha$ -NPD derivative and a PBD derivative are soaked in the diffused solution and left for one night while continuously stirred. Thus, the inorganic phosphor particle 4 to which the  $\alpha$ -NPD derivative and the PBD derivative are chemically adsorbed can be provided.

[0052]

(d) Then, Alq3 was stacked on the phosphor layer 6 by the vacuum evaporation method to form the electron transport layer 7. The film thickness thereof was 50 nm.

(e) Then, Al was stacked on the electron transport layer 7 by the vacuum evaporation method to form the electron injection electrode 8. The film thickness thereof was 200 nm.

(f) Then, it was packaged on the glass substrate with an epoxy adhesive under a circumstances of low moisture and low oxygen concentration to provide the phosphor element.

[0053]

When a DC voltage was applied to the phosphor element manufactured as described above, emission luminance was 400 cd/m<sup>2</sup> at 15V. This was higher than a comparative example 1 which will be shown below. In addition, according to a life test performed on this phosphor element at initial luminance

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of 200 cd/m<sup>2</sup>, a life until the luminance is reduced by half was 18000 hours, which was longer than that of the comparative example 1.

[0054]

(Working example 2)

A display device according to a working example 2 of the present invention will be described with reference to Fig. 4. The display device has a thin film transistor 11 similar to the display device 30 according to the third embodiment, but it is different from the display device 30 in that it has three pixels (R) 41a, (G) 41b, and (B) 41c for colors RGB. The color of the inorganic phosphor particle 4 is varied according to the pixels (R) 41a, (G) 41b, and (B) 41c. In addition, a pixel separating region 42 which separates the pixels is provided in this display device. The pixel separating region 42 includes polyimide and its wall is formed by photo-etching.

[0055]

A description will be made of a manufacturing method of the display device 30. Since the display device 30 is provided such that the phosphor element 10 according to the first embodiment are arranged two dimensionally, it is the substantially the same as that of the phosphor element 10 according to the first embodiment. According to the manufacturing method of the display device, the inorganic phosphor layer 4 which is varied according to the pixels (R) 41a, (G) 41b, and (B) 41c is used. In this case, when the pixel separating region 42 is provided, positioning precision when the pixels 41a, 41b and 41c are formed is improved.

[0056]

(Comparative example 1)

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Similar to the wording example 1, after an electron hole transport layer 3 was formed, a phosphor layer in which 3- (2-benzothiazolyl)-7-diethylaminocoumarin (coumarin 6) is doped in Alq3 was formed by the vacuum evaporation method. Then, similar to the working example 3, the electron transport layer 7 and the electron injection electrode 8 were formed and packaged to provide the phosphor element.

[0057]

When a DC voltage was applied to the phosphor element manufactured as described above, emission luminance was 300cd/m<sup>2</sup> at 7V. In addition, according to a life test performed on this phosphor element under the same initial luminance as that of the working example 1, a life until the luminance is reduced by half was 8,000 hours.

[0058]

(Fourth Embodiment)

A phosphor element according to a fourth embodiment of the present invention will be described with reference to Fig. 5. Fig. 5 is a sectional view showing the phosphor element and perpendicular to its emission surface. The phosphor element 50 is different from the phosphor element according to the first embodiment in that a phosphor direction and a polarity of a driving power supply are reversed, and a stacked constitution of an electron hole injection electrode, an electron injection electrode, an electron hole transport layer and an electron transport layer is reversed according to the polarity of the above drive power supply. In addition, the light is emitted from the side of a transparent substrate 1 as shown by an arrow in the drawing. In addition, since the other components are substantially the same, their description will be

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omitted. According to the phosphor element 50, since the transparent substrate such as the glass substrate used in the first embodiment is set on an upper surface, the light can be emitted from the upper surface without providing a protection layer. In addition, the phosphor element 50 can be formed by bonding the two substrates disposed opposite to each other by the electron hole transport layer or the electron transport layer.

[0059]

(Fifth Embodiment)

A phosphor element according to a fifth embodiment of the present invention will be described with reference to Fig. 6. Fig. 6 is a perspective view showing an electrode constitution of the phosphor element 60. The phosphor element 60 is different from the phosphor element according to the second embodiment in that a phosphor direction and a polarity of a driving power supply are reversed, and a stacked constitution of an electron hole injection electrode and an electron injection electrode is reversed according to the polarity of the above drive power supply, and a thin film transistor 11 connected to an electron injection electrode 8 is provided. In addition, since the other components are substantially the same, their description will be omitted.

[0060]

(Sixth Embodiment)

A display device according to a sixth embodiment of the present invention will be described with reference to Fig. 7. Fig. 7 is a schematic view showing an active matrix of the display device 70, which is constituted by x electrodes 12 and y electrodes 13 intersecting with each other. The display device 70 is different from the display device according to the third embodiment

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in that the plurality of phosphor elements shown in Fig. 6 are arranged two dimensionally. In addition, since the other components are substantially the same, their description will be omitted.

[0061]

(Working example 3)

A working example 3 of the present invention will be described. Since the phosphor element has the same constitution as that of the phosphor element according to the fourth embodiment, a description of its constitution will be omitted. This phosphor element is different from the phosphor element according to the working example 3 in that the phosphor direction and the polarity of the driving power supply are reversed. Therefore, its manufacturing method is different from that of the working example 1.

[0062]

Next, the manufacturing method of this phosphor element will be described with reference to Fig. 5. The phosphor element is manufactured according to the following steps.

- (a) A glass substrate was prepared as a substrate 9 and it was cleaned similar to the glass substrate having the ITO film according to the working example 3.
- (b) Then, MgAg was stacked on the substrate 9 by the vacuum evaporation method to form an electron injection electrode 8. The film thickness was 300 nm.
- (c) CN-PPV was stacked on the electron injection electrode 8 by the vacuum evaporation method to form an electron transport layer 7. The film thickness thereof was 50 nm.
- (d) Then, the inorganic phosphor particle 4 to which the conductive organic

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material 5 was chemically adsorbed was diffused in ethanol using ultrasound and applied to the electron hole transport layer 7 by the spin coat method to form the phosphor layer 6. The film thickness thereof was 150 nm. Thus, a substrate O was provided. Since a manufacturing method of the inorganic phosphor particle 4 to which the conductive organic material 5 is chemically adsorbed is the same as that of the working example 3, its description will be omitted.

(e) Then, as a transparent substrate 1 on which an electron hole injection electrode 2 was formed, a commercially available glass substrate having an ITO film was prepared and cleaned similar to the working example 3.

(f) Then, PEDOT was dissolved with chloroform and applied to the electron hole injection electrode 2 by the spin coat method to form the electron hole transport layer 3. The film thickness thereof was 100 nm. Thus, a substrate P was provided.

(g) Then, immediately after the electron hole transport layer 3 was formed, the phosphor layer 6 of the substrate O of the substrate 9 was put on the electron hole transport layer 3 of the transparent substrate 1 of the substrate P so that the substrate O and the substrate P were bonded. Thus, the phosphor element 50 was provided.

[0063]

When a DC voltage was applied to the phosphor element manufactured as described above, emission luminance was 380cd/m<sup>2</sup> at 16V. This was the same as that of the working example 3.

[0064]

In addition, although a three-layer constitution was illustrated in the



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above description, three or more layers may be provided for the layer containing the organic material.

[0065]

#### EFFECT OF THE INVENTION

As described above, according to the phosphor element having the above constitution of the present invention, the inorganic phosphor material including a low-resistant host crystal, in which a conductive organic material is adsorbed to at least one part thereof is used as the phosphor layer. Thus, there can be provided the phosphor element which can be driven at a voltage as low as that of the conventional organic EL element, and the phosphor element has a long life and high reliability.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view showing a phosphor element and perpendicular to its emission surface according to a first embodiment of the present invention.

Fig. 2 is a perspective view showing a phosphor element according to a second embodiment of the present invention.

Fig. 3 is a schematic plan view showing a display device using a phosphor element according to a third embodiment of the present invention.

Fig. 4 is a sectional view showing a display device using the phosphor element and perpendicular to its emission surface according to the third embodiment of the present invention.

Fig. 5 is a sectional view showing a phosphor element and perpendicular to its emission surface according to a fourth embodiment of the present invention.

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Fig. 6 is a perspective view showing a phosphor element according to a fifth embodiment of the present invention.

Fig. 7 is a schematic plan view showing a display device using a phosphor element according to a sixth embodiment of the present invention.

Fig. 8 is a sectional view showing a display device using the phosphor element and perpendicular to its emission surface according to the seventh embodiment of the present invention.

Fig. 9 is a sectional view showing a conventional organic EL element and perpendicular to its emission surface.

#### REFERENCE NUMERAL

1 transparent substrate, 2 electron hole injection electrode, 3 electron hole transport layer, 4 inorganic phosphor particle, 5 electron transport organic material, 6 phosphor layer, 7 electron transport layer, 8 electron injection electrode, 10 phosphor element, 11 thin film transistor, 12 x electrode, 13 y electrode, 20 phosphor element, 30 display device, 40 display device, 41a pixel (Red), 41b pixel (Green), 41c pixel (Blue), 42 pixel separating region, 50 organic EL element, 60 phosphor element, 70 phosphor element, 80 phosphor element, 90 phosphor element, 100 phosphor element

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Fig. 1

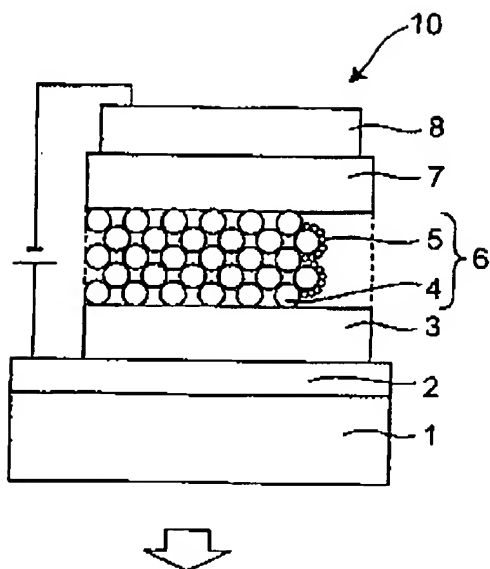


Fig. 2

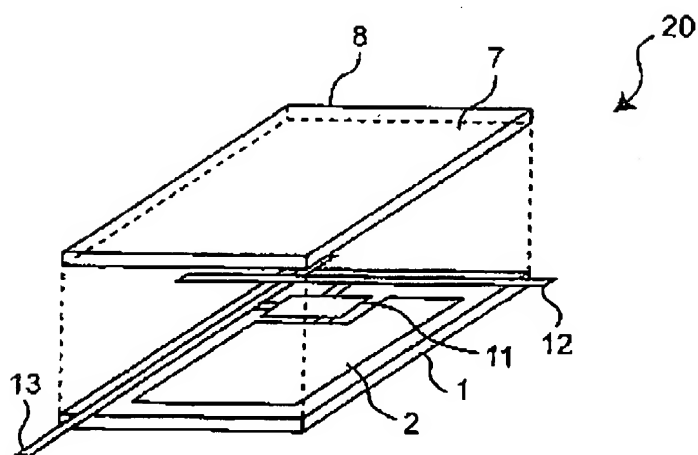


Fig. 3

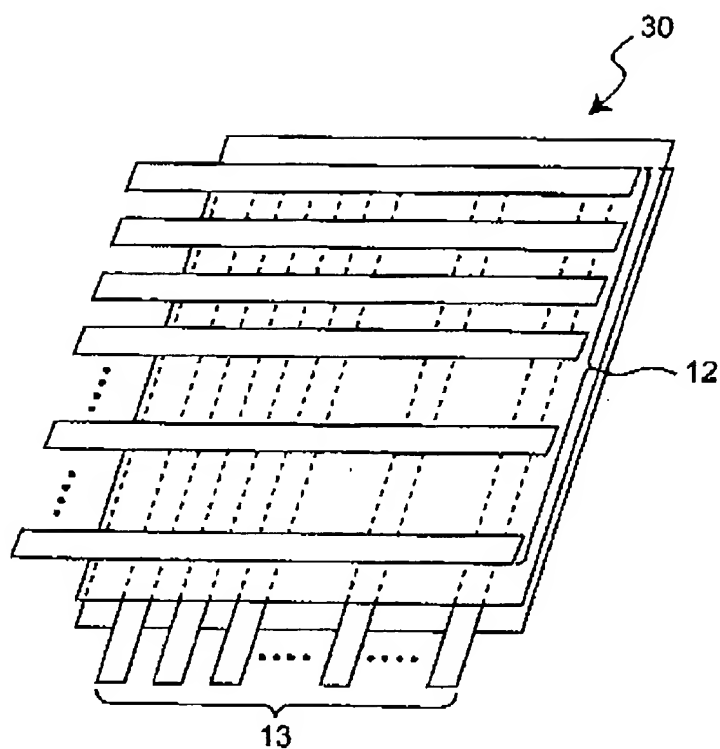


Fig. 4

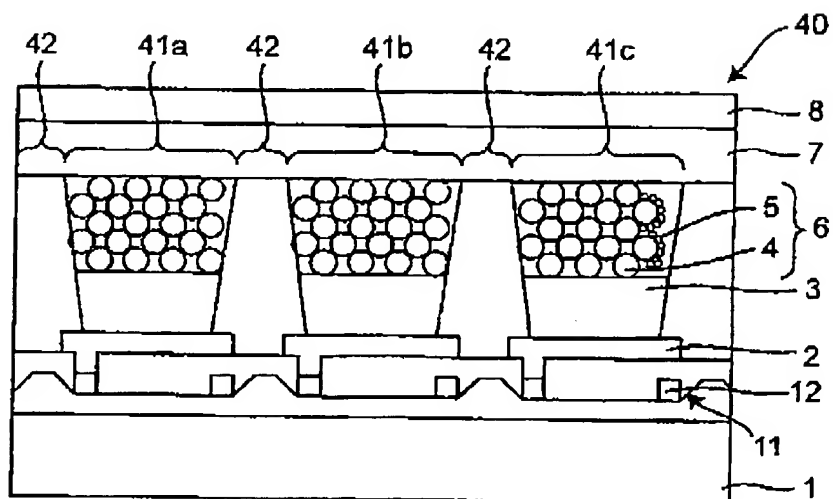


Fig. 5

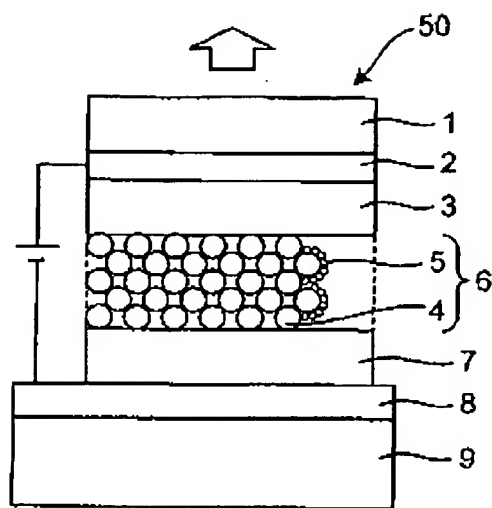


Fig. 6

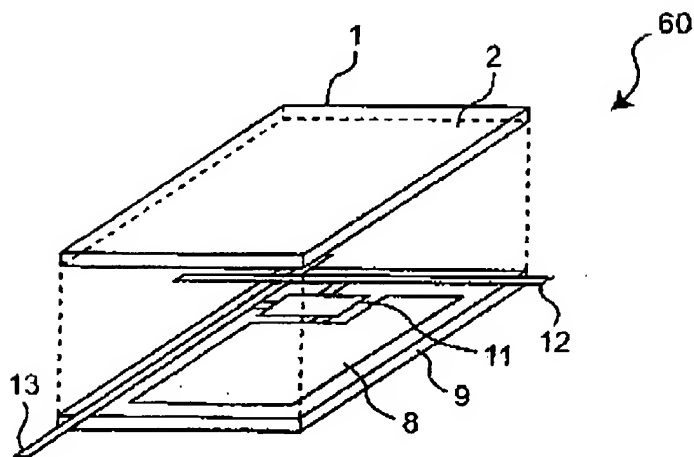


Fig. 7

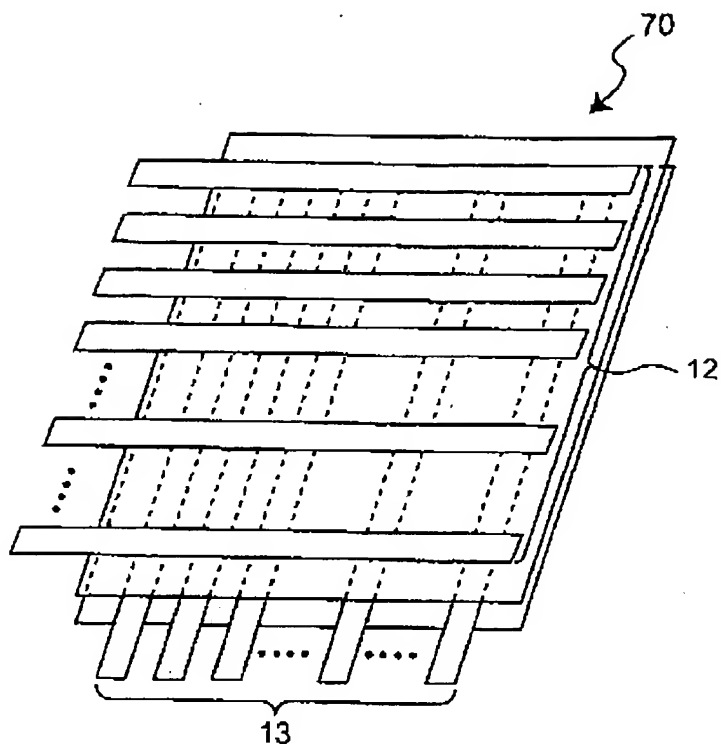


Fig. 8

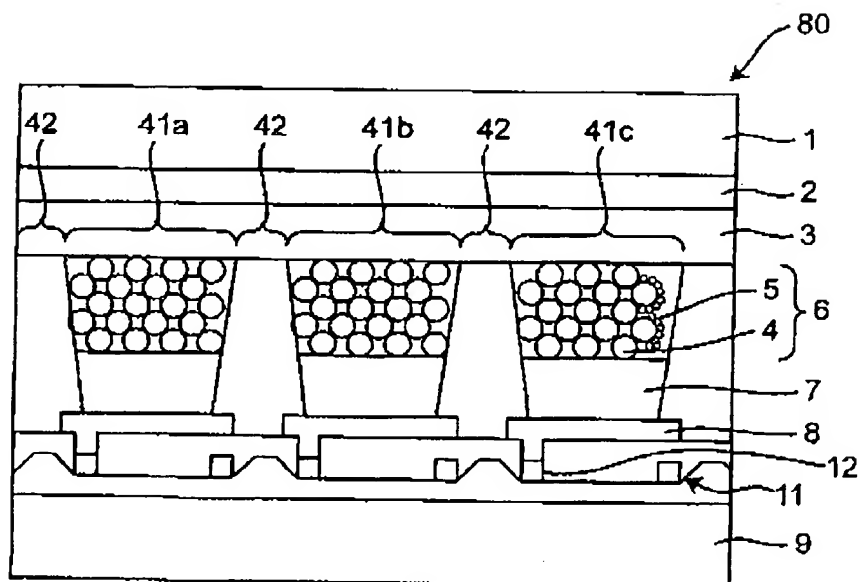
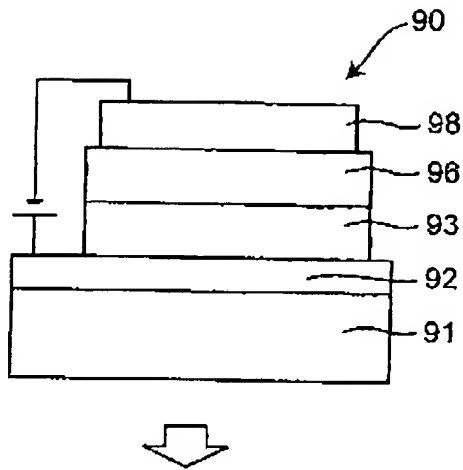


Fig. 9



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DOCUMENT NAME: ABSTRACT

PROBLEM TO BE SOLVED BY THE INVENTION:

It is an object of the present invention to provide a phosphor element having high luminance and a long life which can be driven at low voltage, and a display device using the above phosphor element.

MEANS FOR SOLVING THE PROBLEM:

A phosphor element (10) includes an electron hole injection electrode (2) and an electron injection electrode (8) disposed opposite to each other, an electron hole transport layer (3), a phosphor layer (6), and an electron transport layer (7) stacked in this order from the side of the electron hole injection electrode toward the side of the electron injection electrode. The stacked layers are sandwiched between the electron hole injection electrode and the electron injection electrode, and. The phosphor layer is formed of an inorganic phosphor particle (4) in which at least one part of the surface is covered with an organic material (5).

SELECTED FIGURE: Figure 1